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Vibrational energy is a central aspect of chemical reactivity. Because a few vibrationally energized molecules are the ones that actually overcome the barrier to reaction to form products, the means by which molecules acquire and lose energy is at the heart of chemistry. Thus, vibrationally excited molecules are important in an enormous variety of environments, ranging from the conventional, such as solutions, to the exotic, such as plasmas. We have extended our previous studies of the energy transfer and photodissociation dynamics of isolated molecules into the more complex environment of a liquid with the goal of understanding the role that the solvent plays in the behavior of vibrationally excited molecules. In these experiments, a 100-fs pulse of near or mid-infrared light excites a high frequency stretching vibration of a solute molecule and another short pulse of ultraviolet light monitors the energy content of a subset of the vibrations by transient absorption. The measurements have revealed the influence that vibrational state structure and solvent interactions have on the flow of energy within the vibrationally excited molecule and into the surrounding solvent.

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Energy Transfer and vibrationally Mediated Photodissociation in Liquids

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Abstract

Vibrational energy is a central aspect of chemical reactivity. Because a few vibrationally energized molecules are the ones that actually overcome the barrier to reaction to form products, the means by which molecules acquire and lose energy is at the heart of chemistry. Thus, vibrationally excited molecules are important in an enormous variety of environments, ranging from the conventional, such as solutions, to the exotic, such as plasmas. We have extended our previous studies of the energy transfer and photodissociation dynamics of isolated molecules into the more complex environment of a liquid with the goal of understanding the role that the solvent plays in the behavior of vibrationally excited molecules. In these experiments, a 100-fs pulse of near or mid-infrared light excites a high frequency stretching vibration of a solute molecule and another short pulse of ultraviolet light monitors the energy content of a subset of the vibrations by transient absorption. The measurements have revealed the influence that vibrational state structure and solvent interactions have on the flow of energy within the vibrationally excited molecule and into the surrounding solvent.

INTRODUCTION

Vibrational energy drives chemical reactions in gases and liquids, making vibrationally excited molecules critical actors in environments as diverse as the atmosphere, plasmas, and room temperature solutions. Because vibrations change the relative positions of nuclei in a molecule, reaction requires that enough energy to overcome the barrier to a chemical reaction eventually find its way into a vibration. Consequently, the mechanism and rate of vibrational energy flow within and out of a molecule are central aspects of chemical reactivity. The means by which molecules acquire and lose energy is important not only in chemical reactions but also in the interaction of molecules with light since the spectra and photodissociation dynamics of vibrationally excited molecules can be very different from those of ground state molecules. These considerations have motivated our studies of collisional energy transfer,¹⁻³ energy flow in isolated molecules,⁴ and photodissociation of vibrationally excited molecules.⁵⁻¹³

RECENT RESULTS

The flow of vibrational energy within a molecule and into the surrounding solvent is not only an essential aspect of manipulating vibrationally excited molecules, for example by photodissociating them, but it is also a process that tests theoretical descriptions of couplings within and among molecules. The crucial extension beyond the description of an isolated molecule is inclusion of the solvent and its role in the relaxation. Two limits of intramolecular energy flow are statistical and state-specific energy redistribution. In the limit of uniform, relatively weak coupling to a large collection of vibrational states, the rate of energy flow out of the initially excited state depends on V , the interaction that couples the initially excited state to the other states, and ρ , the density of states, according to the statistical (Fermi's Golden Rule) expression,

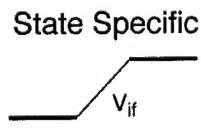
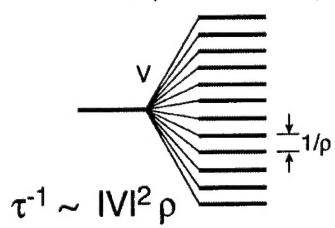


Figure 1

The upper portion of Figure 1 illustrates the coupling of the states in this statistical case. In the limit of state-specific coupling between the initial state $|i\rangle$ and a final state $|f\rangle$, the rate of energy transfer varies as

$$\tau^{-1} \propto |V_{if}|^2 \Gamma(\omega_{if})$$

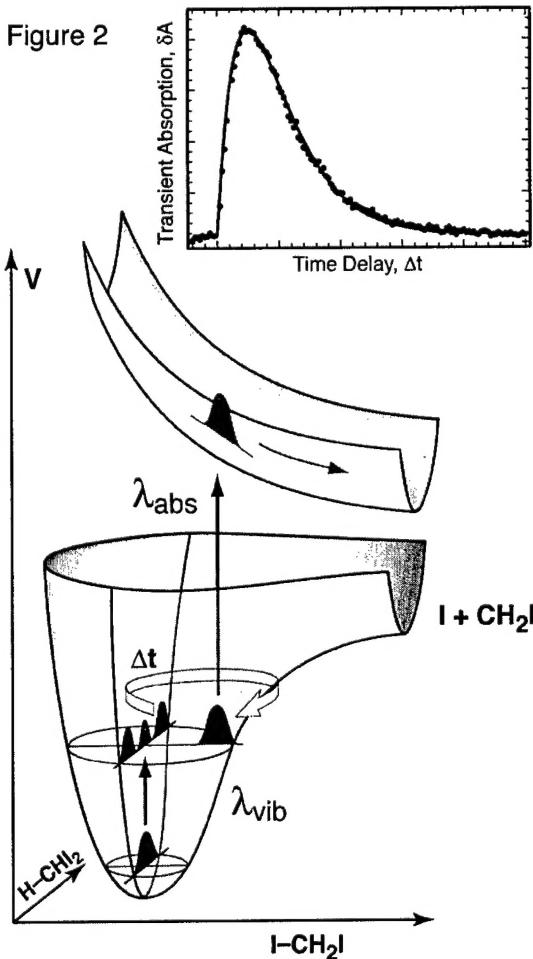
where V_{if} is the coupling between the initial state and final state and $\Gamma(\omega_{if})$ is the spectral density of the solvent evaluated at the energy difference between the initial and final states, as shown in the lower part of the figure.^{14,15} According to the Golden Rule expression, intramolecular vibrational energy redistribution in solvents that alter neither the effective density of states nor the uniform coupling to the background states should be independent of the solvent. (Solvent fluctuations that move some background levels away from the initially excited state simply move others, which have the same interaction, close to the initially excited state.) State-specific relaxation, by contrast, should depend strongly on the solvent, both through the influence of the solvent on the state-to-state coupling, V_{if} , and through the variation in the solvent spectral density, $\Gamma(\omega_{if})$. (Solvent fluctuations change the separation between the two levels as the collective modes of the solvent can make up small energy differences between the initial and final states.) The actual re-

laxation processes are usually more subtle than these limiting cases, but the limits are useful reference points for understanding vibrational energy flow in liquids.

Experimental Approach

The essential feature of our experiments is using an ultrafast infrared or near-infrared laser pulse to create a vibrationally excited molecule and then interrogating it with a second short laser pulse to determine the rates and pathways of energy flow. The diagram in Figure 2 illustrates our approach schematically for the specific case of methylene iodide (CH_2I_2). A roughly 100-fs pulse, generated by optical parametric amplification and non-linear frequency conversion of light from a regeneratively amplified Ti:sapphire laser, excites a C-H stretching vibration. (Two quanta of C-H stretch in the case shown in the figure.) In quantum mechanical terms, it creates a superposition of eigenstates that correspond to the zero-order C-H stretching state (the bright state) that carries the transition strength. Equivalently in classical terms, the short excitation pulse deposits energy in the C-H stretch faster than it can flow into the rest of the molecule.

Figure 2



A second, time-delayed ultraviolet pulse probes the vibrationally excited molecule by exciting it to another electronic state. As illustrated in the figure, the absorption of the second pulse depends on the identity of the excited vibrations. For the probe wavelength shown, the initially excited C-H stretching vibration has a very poor Franck-Condon factor for transition to the excited state, but excitation out of an excited C-I stretching vibration is much more favorable since the separation of surfaces decreases along the C-I stretching coordinate. (Other motions, such as the C-I bend, also enhance the Franck-Condon factor.) Thus, we watch vibrational energy that flows out of the C-H stretch arrive in other modes and then depart into the solvent. The transient absorption trace shown in the figure rises as energy enters the C-I stretch from the initially excited C-H stretch and then falls as the energy goes into the solvent.

The energy transfer experiments begin with 800-nm, 100-fs pulses from the Ti:sapphire laser and use various non-linear frequency conversion schemes to produce pulses ranging from mid-infrared wavelengths near 3 μm to near ultraviolet wavelengths around 300 nm. For example, the transient absorption in Figure 2 is for 380-nm light following excitation of the first C-H

stretching overtone at 1.7 μm. All of our experiments use one or more optical parametric amplifiers (OPA) to convert an 800-nm photon into a pair of longer wavelength photons. These continuum-seeded, double pass devices typically produce up to 100 μJ of near infrared light from a 1-mJ pulse of 800-nm light.¹⁶ Because they are tunable, we obtain different wavelengths of visible and ultraviolet light by frequency doubling or quadrupling their pulses. Generating mid-infrared pulses is more involved, and we

have implemented two different approaches. One is another non-linear technique, difference frequency generation in a AgGaS₂ crystal, that produces infrared light at the difference in the frequency of the signal and idler pulses from our β -barium borate (BBO) OPA.¹⁷⁻²¹ This technique covers a range from about 2.5 μm to 10 μm . The other approach uses 800-nm light to pump a KNbO₃ OPA to produce light in the region of 1 to 4 μm .^{20,22} This approach offers larger pulse energies than difference frequency generation but over a smaller range of wavelengths.

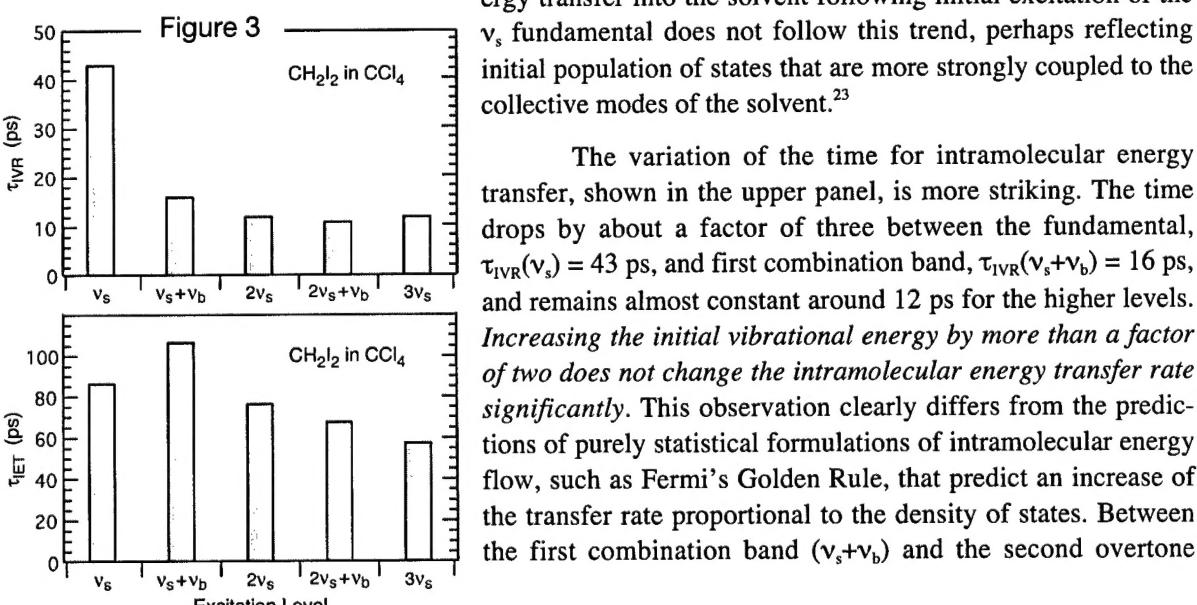
The combination of infrared excitation and ultraviolet probe wavelengths has allowed us to study the relaxation of CH₂I₂ for a range of vibrational states and solvents.²³ We have also used the same approach to study the series of molecules, CH₃I, CH₂I₂, and CHI₃, in which the density of states and interactions among the most strongly coupled states varies substantially.²⁴ These experiments together have produced a detailed picture of the factors that control energy flow and revealed several aspects of the role of the solvent. We have most recently applied the same methodology to monitor energy flow in gas phase molecules in order to discover the behavior in the absence of any solvent, an important point of comparison for intramolecular vibrational energy transfer.

The Influence of Vibrational State Structure on Energy Flow in Liquids

Initial excitation of a fundamental or overtone of the C-H stretch vibration (nv_s) or a combination band with the CH₂ bending vibration ($nv_s + v_b$) followed by observation of the time evolution of the transient electronic absorption allows us to compare the rates of energy flow within CH₂I₂ and then into the solvent for a large range of vibrational energies. The upper panel of Figure 3 shows the rise time of the transient signal, which we identify with the time for intramolecular energy transfer (IVR), τ_{IVR} , and the lower panel shows the decay time, which we associate with the time for intermolecular energy transfer (IET), τ_{IET} , into the solvent for each of five vibrational levels, which span energies from 3000 cm^{-1} to almost 9000 cm^{-1} .

The time for transfer of energy into the solvent varies only modestly with vibrational excitation level. As the lower panel shows, τ_{IET} changes by 25% from its value for the fundamental. Over the range from the first combination band ($v_s + v_b$) to the second overtone of the C-H stretch ($3v_s$), the IET time decreases slightly, indicating moderately faster relaxation for higher total initial energies. The time for energy transfer into the solvent following initial excitation of the

v_s fundamental does not follow this trend, perhaps reflecting initial population of states that are more strongly coupled to the collective modes of the solvent.²³



The variation of the time for intramolecular energy transfer, shown in the upper panel, is more striking. The time drops by about a factor of three between the fundamental, $\tau_{\text{IVR}}(v_s) = 43 \text{ ps}$, and first combination band, $\tau_{\text{IVR}}(v_s + v_b) = 16 \text{ ps}$, and remains almost constant around 12 ps for the higher levels. *Increasing the initial vibrational energy by more than a factor of two does not change the intramolecular energy transfer rate significantly.* This observation clearly differs from the predictions of purely statistical formulations of intramolecular energy flow, such as Fermi's Golden Rule, that predict an increase of the transfer rate proportional to the density of states. Between the first combination band ($v_s + v_b$) and the second overtone

($3\nu_s$), the density of vibrational states increases by a factor of 25, from 4 states/cm⁻¹ to 100 states/cm⁻¹, while the energy transfer time changes by less than a factor of two. Above the energy of the combination band, the energy transfer time does not change at all. Detailed analysis of the state structure suggests that this saturation of the relaxation rate arises from the unimportance of states that are coupled to the initially excited state by high order, and hence generally weak, interactions. Transfer of energy to many of the additional states that are present at higher excitation energies requires exchanging one quantum of C-H stretching vibration for many quanta of a low frequency vibration, such as a Cl₂ bend. These weak, high order interactions do not move energy efficiently on the timescale of energy flow into the solvent. It seems that energy flow through a subset of all the states determines the observed IVR times. We also find that the intramolecular and intermolecular energy flow rates in CH₂I₂ depend on the identity of the solvent.^{23,25,26} Although the absolute rates are different from solvent to solvent, the *relative* change in the rates of both IVR and IET with the level of vibrational excitation is the same, suggesting a similar mechanism for all of the solvents.

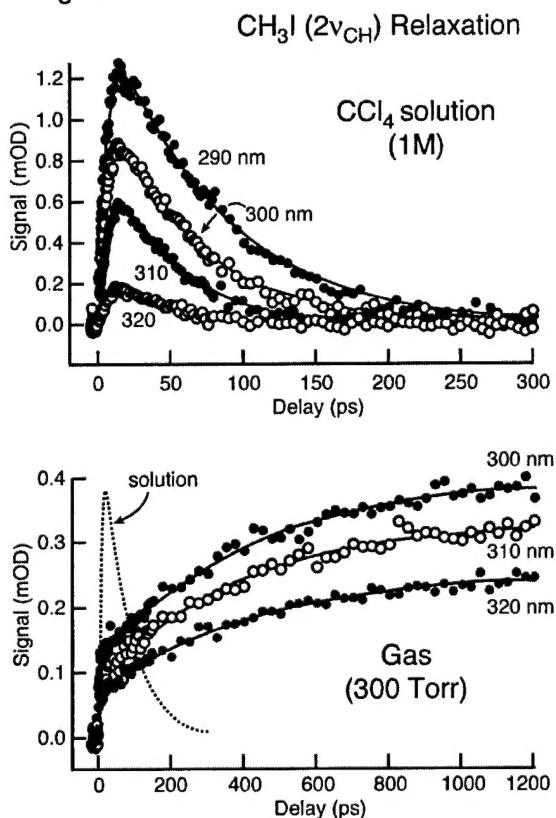
Our study of the vibrational level dependence of the energy flow rate in CH₂I₂ suggests that strong couplings to a restricted number of levels are very important in the relaxation and that the details of the vibrational state structure strongly influence the rate of intramolecular energy flow. Essentially, the measurements on different vibrational levels explore the impact of the density of states by changing the excitation energy. Another means of exploring the role of the state structure in vibrational energy flow is to change the vibrationally excited molecule systematically, an approach we have applied to a series of iodomethanes.²⁴ The density of vibrational states at the energy of the C-H stretch fundamental changes by more than two orders of magnitude for the iodomethanes (CH₃I (0.1 state/cm⁻¹), CH₂I₂ (1 state/cm⁻¹), and CHI₃ (16 states/cm⁻¹)). The increase with iodine substitution comes from the replacement of high frequency modes involving H atoms with low frequency stretching and bending motions involving I atoms. For example, at the 3000 cm⁻¹ energy of the C-H stretching excitation, there are many more possible combinations in the CHI₃ molecule with its low frequency C-I stretches (425 cm⁻¹ and 578 cm⁻¹) and CI₃ deformations (110 cm⁻¹ and 154 cm⁻¹) than in CH₃I with only one C-I stretch mode and no CI₃ deformations.

The intramolecular energy flow would be much faster in CHI₃ than in CH₃I if the total number of vibrational states at the initial excitation energy were the controlling factor. However, the intramolecular energy transfer rates follow exactly the *opposite* trend.²⁴ The IVR rate is *largest* in CH₃I, the molecule with the *smallest* total density of vibrational states. Similarly, it is *smallest* in CHI₃, the molecule with the *largest* density of states. The comparison of the iodomethanes is particularly sharp since the connectivity of the system is the same for all three molecules. The extra states do not come from the addition of substituents that are remote from the initially excited C-H stretch, and the trends again reflect the structure of the strongly coupled states. Enumerating the states and their order of coupling shows that the striking trends in IVR times are parallel to the number of states coupled by low-order (and generally strong) interactions. Thus, we again see that the key to IVR times in these molecules is not the total density of vibrational states but rather the number coupled by low order interactions.

Intramolecular Energy Flow in Isolated CH_3I Molecules

According to the simple, limiting models, solvent interactions should influence the rate of intramolecular energy flow most strongly in molecules or energy levels for which state-specific energy transfer dominates but should play a much smaller or even negligible role in the statistical limit. We have begun exploring the role of the solvent in the intramolecular relaxation by applying the approach we have established in solution to molecules isolated in the gas phase. Thus, we are able to compare the time evolution of a molecule having no interactions with the surroundings to ones interacting with different solvents. We use exactly the same methodology in both cases since our transient electronic absorption probe is sensitive to the arrival of energy in modes such as the C-I stretch that change the Franck-Condon factor. The upper traces in Figure 4 show the transient absorption signal at four different probe wavelengths for a 1 M solution of methyl iodide (CH_3I) in CCl_4 following excitation of two-quanta of the C-H stretching vibration ($2\nu_{\text{CH}}$). The signal has the characteristic rise and fall that we assign to IVR and IET, and their times range from 6 to 9 ps for the rise and 75 to 33 ps for the fall depending on the probe wavelength, behavior analogous to that we observed in CH_2I_2 .

Figure 4



The transient absorption data for a 300 Torr sample of gaseous CH_3I in the lower portion of the figure show several interesting features. The first is simply that the signal is almost as large as that in solution, demonstrating the feasibility of transient absorption studies of molecules with a few hundred Torr of vapor pressure.²⁷ (Obtaining these data, however, requires atypical the stability from our present apparatus.) The second is that the signal does not decay during the 1.2 ns delay covered in the experiment, just as one expects for collisionless molecules and as observed in an earlier study of nitric acid.²⁸ The most interesting feature, however, is that the evolution within the isolated molecule occurs on two different timescales. There is a fast rise in the signal on the order of a ps and a much slower growth that takes about 400 ps. The dotted curve in the lower portion of the figure is the fit to the time evolution in solution. Both the solution and gas phase data have a fast rise that occurs over fewer than 10 ps. (Our first analysis suggests that the rise in solution is actually slightly slower, but that conclusion is quite preliminary.) The fall of the signal in the solution experiment comes from the flow of energy into solution and is much faster (30 to 75 ps) than the slow evolution observable in the isolated molecule. In solution, the relatively rapid dissipation of energy into the solvent would completely mask the slow process.

These new data require more analysis, but there is a simple interpretation that is consistent with our developing picture of vibrational relaxation. The notion of nearly statistical energy flow among a restricted number of relatively strongly coupled states explains several of our observations, such as the variation of the relaxation rate with vibrational level in CH_2I_2 . A simple picture for the gas phase meas-

urements is that the fast rise is that same rapid energy flow among the strongly-coupled states and the slow rise is the subsequent flow of energy into weakly coupled states. If 400 ps were the characteristic time for complete energy redistribution, the energy would never reach those states in solution but would rather leave the molecule and flow into the solvent first. Intermolecular energy flow into the solvent effectively competes with the slowest intramolecular processes.

SUMMARY

Vibrational energy is often the controlling factor in chemical reactions, and the mechanism of energy flow in vibrationally excited molecules is a central aspect of chemical reactivity in environments ranging from room temperature solutions to plasmas and the atmosphere. We have developed time-resolved approaches to following the flow of vibrational energy in a vibrationally excited molecule in liquids as well as gases. These schemes have allowed us to monitor the flow of energy within vibrationally excited molecules and into the solvent. We have even compared the flow of energy in an isolated molecule to the flow of energy in the same molecule in solution. These experiments open up the possibility of recapitulating detailed gas phase studies of vibrational excitation and photodissociation in the more complex environment of a liquid with the goal of understanding the influence of the solvent on vibrational energy flow and the interaction of vibrationally excited molecules with light.

AFOSR SUPPORTED PUBLICATIONS

Transient Electronic Absorption of Vibrationally Excited CH₂I₂: Watching Energy Flow in Solution. Dieter Bingemann, Andrew M. King, and F. Fleming Crim, J. Chem. Phys. **113**, 5018 (2000).

Relaxation of the C-H Stretching Fundamental Vibrations of CHI₃, CH₂I₂, and CH₃I in Solution. Max M. Heckscher, Leonid Sheps, Dieter Bingemann, and F. Fleming Crim, J. Chem. Phys. **117**, 8917 (2002).

Vibrational Relaxation of CH₂I₂ in Solution: Excitation Level Dependence. Christopher G. Elles, Dieter Bingemann, Max M. Heckscher, and F. Fleming Crim, J. Chem. Phys., **118**, 5587 (2003).

Vibrational Relaxation of CH₃I in the Gas Phase and in Solution. Christopher G. Elles, M. Jocelyn Cox, and F. Fleming Crim, J. Chem. Phys. (*in press*)

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